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(54) Process for producing a cellulose ester solution and film

(57) A cellulose ester, e.g. triacetate, is made by acetylating cellulose and neutralizing residual sulfuric acid with an alkaline earth metal acetate. Residual metal is removed by dissolving the ester in glacial acetic acid, filtering and drying. The content of alkaline earth metal is thus reduced to no more than 30 ppm.

The ester is then dissolved, with a plasticiser, in an organic solvent; the solution is extruded onto a moving support to form a film, which is useful as a support for a photographic material.

The removal of the salt reduces the viscosity of the solution and makes the extrusion of the film easier.

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SPECIFICATION

Process for producing a cellulose ester solution and film

This invention relates to a process for producing a cellulose ester solution and to a process for producing a cellulose ester film from the resultant organic solvent solution of a cellulose ester having a low viscosity.

Cellulose esters such as cellulose acetate, cellulose butyrate and cellulose acetate propionate have been used as supports in photographic light-sensitive materials. Cellulose triacetate is extensively used, due to its excellent characteristics such as dimensional stability, transparency and luster.

A process for producing cellulose triacetate film from a solution is conducted as follows. Cellulose acetate, usually having a bound acetic acid content of 56% or more, is dissolved in a mixed solvent of a lower hydrocarbon chloride (for example, methylene chloride) and a lower aliphatic alcohol (for example, methanol, ethanol, *n*-propanol, isopropanol or *n*-butanol). A suitable plasticizer and, in some cases, a dye are added thereto. The resulting solution is subjected to purifying steps such as filtration, defoaming and adjustment to viscosity (concentration), temperature, etc., then fed to a filming machine. The purified solution is extruded in a film form onto a moving support by means of a suitable film-forming machine (this procedure being generally referred to as casting procedure, and moving support being a surface of a rotary drum or endless belt). The solvent is evaporated from the solution film during almost one rotation of the support. The thus formed film is delaminated from the support surface and dried in a suitable drying machine to evaporate the remaining solvent from the delaminated film.

Therefore, when producing cellulose triacetate film, it is quite advantageous from the industrial point of view that the cellulose triacetate starting material readily forms a uniform solution, that the cellulose triacetate solution permits a plasticizer and a dye added thereto to be readily and uniformly mixed therein, that the solution can be easily filtered and defoamed, that the solution can be easily extruded from the film-forming machine onto the moving support and that the solvent used can be easily evaporated from the solution film.

One method for attaining the above-described advantages is reduction of the viscosity of the cellulose triacetate solution.

In general, the viscosity of the cellulose triacetate solution can be reduced by decreasing the degree of polymerization of the cellulose triacetate starting material and/or by decreasing the concentration of its solution. However, reduction of the degree of polymerization of the cellulose triacetate starting material is accompanied by deterioration of the mechanical strength of the film prepared therefrom, and so is not advantageous.

A decrease in the concentration of the cellulose triacetate solution requires a high drying temperature and/or a long drying time in the solvent-evaporating step after the casting; due to the increased use of energy and time this is also disadvantageous.

Thus, a cellulose triacetate solution with a high viscosity is usually used. However, this leads to the following difficulties in production:

(1) Stirring efficiency, when preparing the cellulose triacetate solution, is so poor that it takes a long time to obtain a uniform solution.

(2) Upon addition of a plasticizer and a dye to the solution, a long time is required to obtain uniform mixing.

(3) Piping must be used which has a large diameter, due to the high resistance of the solution in the pipes; this requires a wide space to be left between the pieces of equipment.

(4) A solution-ejecting pump of high power must be used for transporting the solution.

(5) In filtering the solution to remove foreign matter (e.g. insoluble cellulose triacetate or dust), high pressure must be applied and so a tough, pressure-resistant equipment and a powerful solution-ejecting pump must be used.

Points (3) to (5) cause an increase in the cost of the equipment and production. The application of an increased filtering pressure can result in gushing out of the solution, which is unsafe.

(6) When defoaming the solution, the temperature of the solution is raised and/or pressure is applied thereto, which can also cause gushing out of solution. Defoaming the solution by allowing it to stand requires a long period of time.

(7) When extruding the solution from a film-forming machine onto a moving support, an increase in extrusion speed causes disturbance in the stream of solution in the film-forming machine, and the surface of the solution film is difficult to be levelled. Thus the resulting film canot be used. The resulting film is particularly unsuited as a support for photographic light-sensitive material. Therefore, the extrusion speed must be reduced to such a degree that no disturbance takes place in the solution, which is industrially quite disadvantageous.

The above-described disadvantages are also encountered when using other cellulose esters.

An object of the present invention is to provide a process for producing a cellulose ester solution having a low viscosity, without reducing the degree of polymerization of the cellulose ester starting material and without decreasing the concentration of the cellulose ester solution, and preferably by using a solution permitting high speed film formation, whereby there can be obtained a support having excellent mechanical strength and a highly uniform surface, and which does not adversely affect photographic properties when it

is used as a support for photographic materials.

The inventors have found that the content of alkaline earth metal in the cellulose ester is an important factor affecting the viscosity of the cellulose ester solution.

The present invention relates to a process of producing a solution from which a film of a cellulose ester may be cast, the ester having been produced by a reaction wherein an alkline earth salt was added to neutralise acidic reactants, which process comprises reducing the content of alkaline earth metal in the cellulose ester to not more than 30 parts per million, and dissolving the ester in an organic solvent together with a plasticizer.

In general, cellulose triacetate produced by a process for producing a cellulose triacetate support, for example, an acetic acid process, contains 50 to 100 ppm alkaline earth metal. The acetic acid process is a process which comprises adding acetic anhydride and sulfuric acid to cellulose to acetylate cellulose, then neutralizing residual sulfuric acid with an alkaline earth metal salt such as calcium acetate or magnesium acetate; the cellulose acetate produced by the acetic acid process therefore contains an alkaline earth metal such as calcium or magnesium. Surprisingly, we have found that the viscosity of the cellulose triacetate solution is remarkably reduced by decreasing the content of the alkaline earth metal to 30 ppm or less; within the range of 0 to 30 ppm of alkaline earth metal, the viscosity of the solution is proportional to the content of the alkaline earth metal.

For the cellulose ester it is preferable to use cellulose acetate, cellulose acetate butyrate or cellulose acetate propionate. Of these, cellulose acetate having a degree of polymerization (number of monomer units) of 250 to 400 and a bound acetic acid content (degree of acetylation) of 54 to 62% is particularly preferable.

The plasticizers include triphenyl phosphate, biphenyldiphenyl phosphate, dimethoxyethyl phthalate and ethylphthalylethylene glycol. None of these plasticizers reduce the advantageous effects of the present invention.

The plasticizers are used preferably in amount of 5 to 20 weight % based on the weight of the cellulose ester.

Preferred solvents which can be used include lower aliphatic hydrocarbon chlorides such as methylene chloride, and lower aliphatic alcohols such as methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol and *n*-butanol. Methanol and ethanol may be used alone or in combination with e.g. *n*-butanol. As to solvent proportion, 80 to 100 weight % methylene chloride and 0 to 20 weight % lower aliphatic alcohol are preferably employed.

The concentration of the cellulose ester in the solution is preferably 10 to 50 weight %.

If necessary, in the cellulose ester solution additives may be included, such as an alkaline earth metal-free dye or another polymer soluble in the aforesaid solvents.

Residual alkaline earth metal can be removed from cellulose acetate to a degree of 30 ppm or less by the following method. 10 g of cellulose triacetate is dissolved in 1,000 g of glacial acetic acid. Then 1,000 g of water is added to the acetic acid solution with stirring to precipitate cellulose triacetate; the precipitate is collected by filtration and dried at 110°C for 24 hours.

Example

Two cellulose acetates were prepared by the aforesaid acetic acid process; each acetylated cellulose was neutralised with magnesium acetate, and calcium acetate was then incorporated.

Both products were divided into four samples, three of which were treated with glacial acetic acid, as just described, once or several times, whereby varying amounts of the residual magnesium and calcium were removed.

To each of the cellulose acetate samples was added a (3:1 by weight) mixture of triphenyl phosphate and biphenyldiphenyl phosphate as a plasticizer in an amount of 10 weight % of the cellulose acetate. Then, a solution containing 20 weight % of cellulose acetate was prepared from each sample in a mixed solvent of methylene chloride and methanol (9:1 by weight). The viscosity of each solution was measured at 20°C with a falling ball viscometer.

[Falling ball viscometer: steel ball: 5/16 inch; specific gravity: 7.78; glass cylinder: 1.00 inch in inside diameter; falling distance: 10.0 inches]

		Degree of Polymerization	*Degree of Acetylation*	*Content of Alkaline Earth metal (ppm)*	*Viscosity (poise)*
Sample	A	300	61.0	87	1300
	B	300	61.0	35	1230
	C	300	61.0	30	700
	D	300	61.0	4	620
	E	250	61.5	50	620
	F	250	61.5	35	600
	G	250	61.5	30	310
	H	250	61.5	4	280

Samples B, C and D were prepared by treating sample A by the method described hereinbefore to remove alkaline earth metal.

Samples F, G and H were prepared by treating sample E as described hereinbefore to remove alkaline earth metal.

Comparison of sample A with sample B reveals that, even though the content of alkaline earth metal was reduced from 87 ppm to 35 ppm, the viscosity was changed only from 1300 poises to 1230 poises. However, when the content of the alkaline earth metal was reduced to 30 ppm in sample C, the viscosity surprisingly became about half of that of sample A.

Comparison of sample E with sample F reveals that, even though the content of alkaline earth metal was reduced from 50 ppm to 35 ppm, the viscosity was changed only from 620 poises to 600 poises. However, when the content of the alkaline earth metal was reduced to 30 ppm in sample G, the viscosity surprisingly became about half of that of sample E.

Sample D having the degree of polymerization of 300 showed the same viscosity as that of sample E having the degree of polymerization of only 250.

When samples D and E were cast by extrusion of solution through a T-die, the dope stream-disturbing speed of sample D was 50 m/min., which was the same as that of sample E in spite of the fact that the degree of polymerization of sample D was higher than that of sample E by 50.

However, mechanical properties of the film obtained by casting sample E were inferior to those of the film obtained by casting sample D as shown below.

	Tear Strength (g/100 μ)	*Folding Endurance* (times/100 μ)
Sample D	42 g (n=7)	83 times
E	35 g (n=7)	55 times

	Breaking Stress (Kg/mm^2)	Breaking Extension (%)
Sample D	11.5	40
E	11.5	35

Additionally, when the cellulose acetate film of the present invention was coated, after undercoating, with a silver halide color photographic emulsion, no detrimental influences on photographic properties of the emulsion were observed.

CLAIMS

1. A process of producing a solution from which a film of a cellulose ester may be cast, the ester having been produced by a reaction wherein an alkaline earth salt was added to neutralise acidic reactants, which process comprises reducing the content of alkaline earth metal in the cellulose ester to not more than 30 parts per million, and dissolving the ester in an organic solvent together with a plasticizer.
2. A process according to Claim 1, wherein the alkaline earth metal content is reduced by dissolving the ester in acetic acid, adding water to precipitate the ester and recovering the precipitate.
3. A process according to Claim 1 or 2, wherein the solvent is an aliphatic hydrocarbon chloride or alkanol having up to 4 carbon atoms.
4. A process according to Claim 1, 2 or 3, wherein the ester is cellulose ester containing 250 to 400 monomer units and 54 to 62% by weight of bound acetic acid.
5. A process according to any preceding claim, wherein the plasticizer comprises 5 to 20 weight % of the cellulose ester.
6. A process according to any preceding claim, wherein the concentration of the cellulose ester in solution is 10 to 50 weight %.
7. A process of producing a solution as claimed in Claim 1, substantially as hereinbefore described with reference to sample C, D, G or H of the Example.
8. A solution prepared by a process as claimed in any preceding claim.
9. A process of producing a film of a cellulose ester, which comprises extruding a solution as claimed in Claim 8, allowing the solvent to evaporate, and removing and drying the resultant film.
10. A film produced by the process as claimed in Claim 9.
11. A silver halide color photographic material which includes as a support a film of a cellulose ester as claimed in Claim 10.

New claims or amendments to claims filed on 11th June 1982
Superseded claims 3
New or amended claims:-

3. A process according to Claim 1 or 2, wherein the solvent is an aliphatic hydrocarbon chloride or aliphatic alcohol having up to 4 carbon atoms.

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